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VIII.

CONTRIBUTION FROM THE SALISBURY LABORATORY OF THE WORCESTER POLYTECHNIC INSTITUTE.

ON THE FORMATION OF THE ANHYDRIDES OF BENZOIC AND SUBSTITUTED BENZOIC ACIDS.

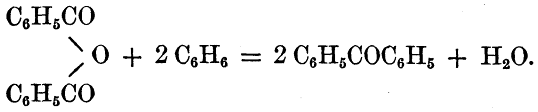
By George D. Moore and Daniel F. O'Regan.

Presented by Professor L P Kinnicutt, April 13, 1892.

By the action of phosphoric anhydride upon benzoic acid and an excess of benzol at 180–200°, Kollarits and Merz * obtained benzophenone. The course of the reaction is shown by the following equation:

$$C_6H_5COOH + C_6H_6 = C_6H_5COC_6H_5 + H_2O.$$

The same result was also obtained when, instead of benzoic acid, benzoic anhydride was employed:



$$\begin{matrix} C_6H_5CO \\ C_6H_5CO \end{matrix} \Big> O + 2\,C_6H_6 = 2\,C_6H_5COC_6H_5 + H_2O.$$

In a second paper † on this subject, the same authors state that the formation of benzoic anhydride may possibly precede that of benzophenone, and add that, if such is the case, benzophenone must be formed by the direct action of benzoic anhydride upon benzol, even in absence of phosphorpentoxide. This last result they were unable to effect, even at temperatures ranging as high as 300°. Similar negative results were likewise obtained when toluol was employed instead of benzol. They therefore conclude that benzophenone is the product of the direct action of phosphorpentoxide upon benzoic acid and benzol.

The following experiments were undertaken with a view to studying more carefully the conditions of possible formation of

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* Zeitschr. für Chemie, 1871, p. 705. Berichte, V. 447.

† Berichte, VI. 537.

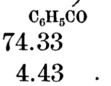
anhydrides as intermediary products in the synthesis of ketones from benzoic and substituted benzoic acids and hydrocarbons. If anhydrides are formed at all, it is reasonable to suppose that the reaction takes place at a temperature comparatively lower than that required for the ketone condensation; and we find that this is in fact the case.

I. *Action of Phosphorpentoxide upon Benzoic Acid in an Excess of Benzol.*

10 grams of benzoic acid, previously melted, pulverized, and thoroughly dried, were dissolved on the steam bath in about 200 c.c. of dry benzol, 10 grams phosphorpentoxide added to the hot solution, and the whole boiled under a reverse condenser for about four hours. The phosphorpentoxide did not appear to dissolve, but settled to the bottom of the flask in the form of an amorphous, gelatinous mass, which became gradually darker, until at the end of the operation, it was nearly black.

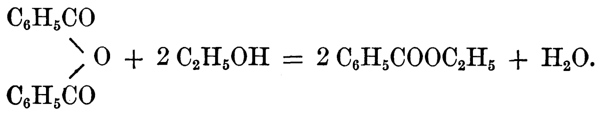
The supernatant benzol solution was of a light amber color. It was filtered hot from the insoluble residue, and, as no precipitate was deposited after standing over night, concentrated to about one third of its volume. On cooling, this solution threw down a copious precipitate of fine white needles, which were freed from the benzol mother-liquor by pressing between filter-paper, washed with dilute potash solution to remove possible traces of benzoic acid, and the residue taken up in ether. After one or two washings with water, the ether solution was drawn off, and the residue, after distilling off the ether, dissolved in ligroine. From this it crystallized in fine prismatic needles melting at 41–42°. On analysis the substance gave the following values: —

0.2153 grm. gave 0.5832 grm. CO_2 and 0.0903 grm. H_2O.

	Calculated for  $\begin{matrix}C_6H_5CO\\C_6H_5CO\end{matrix}\!>O.$	Found
C	74.33	73.87
H	4.43	4.60

The melting point and composition of the body show it to be without doubt benzoic anhydride, and the study of its properties confirms this conclusion. It consists of fine, prismatic, needle-like forms, easily soluble in alcohol, ether, benzol, chloroform and carbon disulphide, difficultly in water and in petroleum ether. This last is the best medium for its crystallization. Cold water converts it slowly, boiling water rapidly, into benzoic acid. Alkalies transform it into benzoic acid salts, from the solutions of which mineral acids precipitate benzoic acid in its characteristic leaflets.

The gelatinous phosphoric anhydride residue from the original benzol solution gave on extraction with benzol only a trace of anhydride. As this extract did not appear to contain any other substance, the gelatinous residue was taken up in absolute alcohol, with a view of thus isolating any benzophenone which might have been formed. As the alcohol was poured upon the residue, considerable heat was manifested. The alcoholic solution was concentrated to a small volume, but no crystals could be obtained. After some days, the alcohol having entirely disappeared, there remained in the beaker a small quantity of a pleasant-smelling, oily liquid. This was taken up in water to remove the phosphoric acid, washed with dilute potash to remove benzoic acid, and extracted with ether. Finally there remained a few drops of a brownish-colored oil, which, from its odor, we concluded was benzoic ethyl ester. Unfortunately the amount was too small and too impure to admit of analysis. Its formation may be ascribed to the following reaction: —



$$\left.\begin{matrix}C_6H_5CO\\ \\ C_6H_5CO\end{matrix}\right\rangle O + 2\,C_2H_5OH = 2\,C_6H_5COOC_2H_5 + H_2O.$$

It is probable that the anhydride necessary for this reaction was retained, mechanically enclosed, in the gelatinous phosphorous residue, from which it is but incompletely extracted by treatment with benzol. Phosphoric anhydride being readily soluble in alcohol, the formation of the ester is easily accounted for. In subsequent experiments we obtained some more of this oil, which boiled between 215° and 225°, (benzoic ethyl ester boils at 211–212°,) but could not get it in sufficiently large quantity to purify for analysis. The formation of esters of the nitrobenzoic acids, as described hereafter, under similar conditions, render it practically certain that the substance we have just described is benzoic ethyl ester.

II. *Action of Phosphorpentoxide upon Orthonitrobenzoic Acid in an Excess of Benzol.*

10 grams *o*-nitrobenzoic acid, melting point 147°, were dissolved in about 200 c.c. of pure, dry benzol, 10 grams phosphorpentoxide

added to the hot solution, and the whole boiled on the steam bath for about three hours. As with benzoic acid, the phosphorpentoxide did not dissolve, but settled to the bottom of the flask as an amorphous, gelatinous mass, which became gradually darker-colored as the heating progressed, until, at the end of the operation, it was almost black. The amber-colored, supernatant liquid was decanted hot through a plaited filter and allowed to crystallize. After standing over night it had thrown down a considerable quantity of large, feather-shaped crystals, which, as their amount did not appear to increase on longer standing, were filtered, and washed with dry benzol. Their melting point, 147°, and ready solubility in alkalies, as well as their characteristic sweet taste, showed them to be the unchanged *o*-nitrobenzoic acid.

The mother-liquor from these crystals was concentrated to about one third of its original volume and allowed to stand. The result was a precipitate of short, thick, prismatic crystals, entirely different from the feather-shaped forms of the nitro acid, and melting at 128° to 130°. By repeated crystallization from benzol, this melting point was raised to 133°, at which temperature it remained constant. The analyses gave the following results: —

0.3393 grm. substance gave 25 c.c. nitrogen at 3.2° and 749.8 mm.
0.2564 grm. substance gave 0.5016 grm. CO_2 and 0.0700 grm. H_2O.

	Calculated for $\begin{array}{l}\mathrm{C_6H_4}\left\{\begin{array}{l}(1)\,\mathrm{NO_2}\\(2)\,\mathrm{CO}\end{array}\right.\\ \qquad\quad\rangle\,\mathrm{O.}\\ \mathrm{C_6H_4}\left\{\begin{array}{l}(2)\,\mathrm{CO}\\(1)\,\mathrm{NO_2}\end{array}\right.\end{array}$	Found.
C	53.16	53.34
H	2.53	3.03
N	8.86	8.96

In its properties the substance agrees with those assigned to the anhydride of orthonitrobenzoic acid by Bischoff and Roch,* viz. difficultly soluble in water and ether, more readily in alcohol, benzol, and glacial acetic acid. Heated quickly upon platinum foil it explodes. Continued treatment with boiling water or with alkalies converts it into the acid. Bischoff and Roch place the melting point of the anhydride at 135°, while we have not been able to raise it above 133°.

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* Berichte, XVII. 2789.

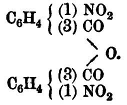
The phosphoric anhydride residue from which the benzol solution of *o*-nitro acid and anhydride had been decanted, yielded only a small amount of the acid on being extracted with fresh benzol. As a considerable quantity of insoluble residue still remained after repeating the operation, we substituted absolute alcohol for benzol as an extracting agent. With this we obtained a clear solution which was evaporated to dryness, washed with cold water until free of phosphorus, and recrystallized from alcohol. The product consisted of small tablets which melted at 30°, and is in all probability the ethyl ester of orthonitrobenzoic acid. The amount was too small for an analysis.

III. *Action of Phosphorpentoxide upon Meta Nitrobenzoic Acid in an Excess of Benzol.*

10 grams *m*-nitrobenzoic acid were dissolved in about 200 c.c. dry benzol, 10 grams of phosphorpentoxide added to the hot solution, and the whole boiled for three to four hours on the steam bath under a reverse condenser. As in the previous experiments, the phosphorpentoxide did not dissolve, but settled to the bottom of the flask as a thick, gummy mass, which, as the boiling continued, became rapidly darker-colored.

The supernatant liquid was decanted hot through a plaited filter, the residue in the flask boiled with fresh benzol, and this extract added to the first. The solution immediately threw down a precipitate of fine white needles, which, after drying, showed a melting point of 161°, which was not raised by recrystallization from benzol. Dried at 110° the substance analyzed as follows: —

0.3051 grm. gave 0.5871 grm. CO_2 and 0.0548 grm. H_2O.
0.2032 grm. gave 0.3904 grm. CO_2 and 0.0611 grm. H_2O.
0.2166 grm. gave 0.4160 grm. CO_2 and 0.0608 grm. H_2O.
0.3875 grm. gave 28.6 c.c. nitrogen at 6.6° and 748 mm.
0.4021 grm. gave 32.6 c.c. nitrogen at 4.2° and 755.7 mm.

	Calculated for  $\left.\begin{matrix} C_6H_4\left\{\begin{matrix}(1)\ NO_2\\(3)\ CO\end{matrix}\right. \\ C_6H_4\left\{\begin{matrix}(3)\ CO\\(1)\ NO_2\end{matrix}\right.\end{matrix}\right\rangle O.$		Found.	
		I.	II.	III.
C	53.16	52.48	52.40	52.37
H	2.53	2.00	3.34	3.14
N	8.86	8.82	8.70	

The complete combustion of the body is an exceedingly difficult operation. The substance must be thoroughly mixed with the oxide of copper or lead chromate, and burned very slowly in a generous current of oxygen. Even under these conditions the values for carbon are quite low. The chemical relations of the body, however, leave no doubt that it is the anhydride of meta nitrobenzoic acid. It dissolves readily in dilute alkalies in the cold, and from such solution mineral acids precipitate the meta acid, easily identified by its melting point, 141°, and crystalline form.

Meta nitrobenzoic anhydride is readily soluble in alcohol, ether, and chloroform, less readily in benzol (from which solvent it crystallizes best), and difficultly in water. Cold water has but little effect upon it, boiling water decomposes it rapidly into the free acid.

From the gelatinous phosphoric residue by extraction with absolute alcohol, evaporating to dryness, and taking up with water, a product was obtained which crystallized from alcohol in small rhombic plates, melting at 42°. The same body was obtained by treating the anhydride with absolute alcohol and phosphorpentoxide. Its melting point and method of formation show it to be the meta nitrobenzoic ester.

IV. *Action of Phosphorpentoxide upon Para Nitrobenzoic Acid in an Excess of Benzol.*

Para nitrobenzoic anhydride is the principal product when para nitrobenzoic acid and phosphorpentoxide are boiled together for some hours in an excess of dry benzol. The proportions employed were the same as with the ortho and meta nitro acids.

The anhydride crystallizes from benzol in white leaflets melting at 184°. The analyses gave the following: —

0.1716 grm. substance gave 0.3311 grm. CO_2 and 0.0530 grm. H_2O.
0.3461 grm. gave 25.6 c.c. nitrogen at 4.6° and 746.5 mm.

	Calculated for $\left.\begin{matrix}C_6H_4\left\{\begin{matrix}(1)\,NO_2\\(4)\,CO\end{matrix}\right.\\ C_6H_4\left\{\begin{matrix}(4)\,CO\\(1)\,NO_2\end{matrix}\right.\end{matrix}\right\rangle O.$	Found.
C	53.16	52.61
H	2.53	3.40
N	8.86	8.90

Like the isomeric ortho and meta bodies, the para nitrobenzoic anhydride is an exceedingly difficult substance to burn. It is but slightly soluble in alcohol, ether, benzol and carbon disulphide in the cold, readily however on warming. In ligroine and water it is insoluble. Continued boiling with water converts it into the acid. Alkalies produce the same effect, slowly in the cold, more rapidly on heating.

As in the case of the other nitro-anhydrides the phosphoric residue gave, on extraction with absolute alcohol, the para nitrobenzoic ethyl ester. This may be more readily obtained by boiling the anhydride with phosphorpentoxide in absolute alcohol solution.

It is proposed to extend the study of this phosphorpentoxide reaction to other substituted benzoic acids.